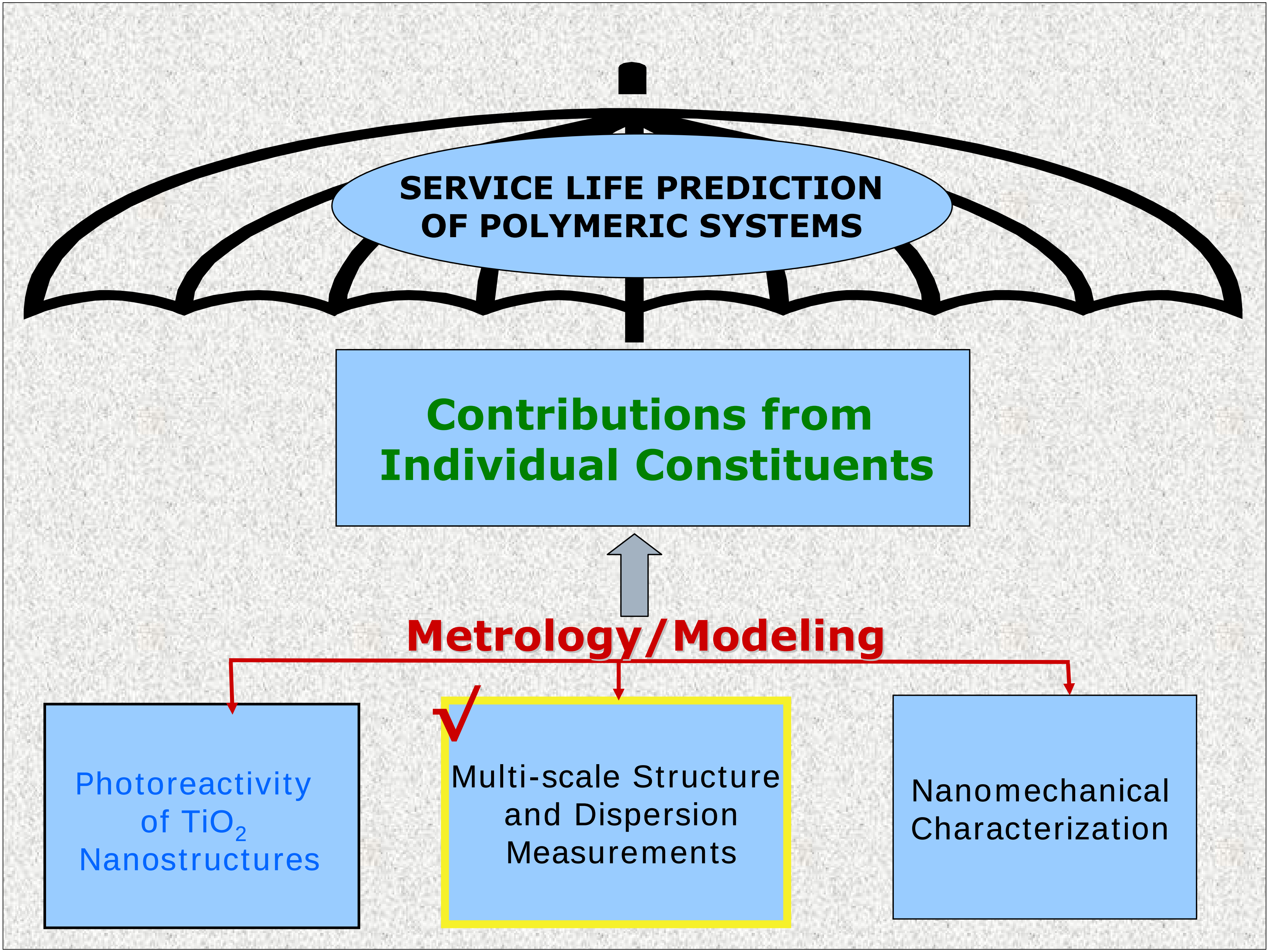
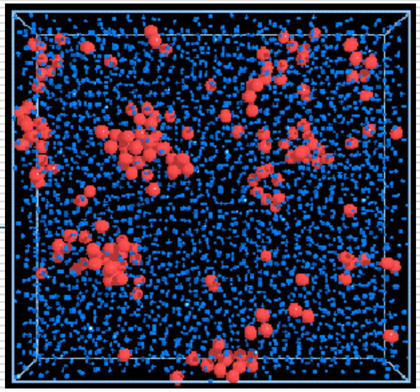

SERVICE LIFE PREDICTION
OF POLYMERIC SYSTEMS
Contributions from
Individual Constituents
Metrology/Modeling
Photoreactivity
of TiO_2
Nanostructures
√
Multi-scale Structure
and Dispersion
Measurements
Nanomechanical
Characterization

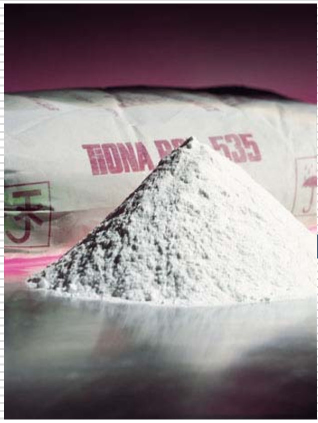
Multi-scale Structure and Dispersion Measurements of Polymeric Coatings and Plastics

Li-Piin Sung



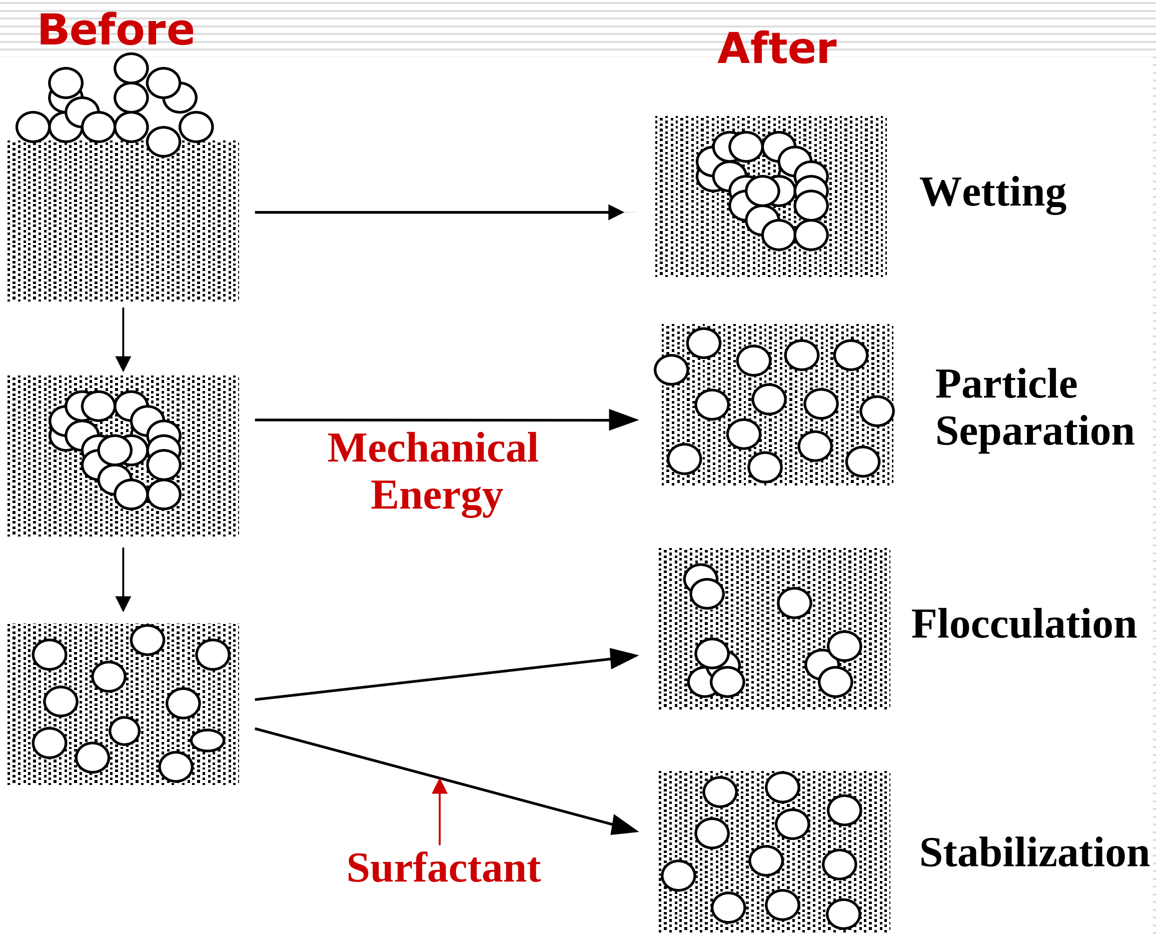
The Problem

- Almost all commercial polymeric construction products contain dispersed pigmentary and nanoscale particles.
- Poor particle dispersion adversely creates multi-scale structure in products, and affects service life, appearance, and mechanical properties of these products.
- Current industrial methods for assessing particle dispersion are subjective, unreliable, and limited to dilute suspensions of micron-size particles.
- Industrial needs: systematic understanding and efficient tools for measuring and controlling dispersion.



Dispersion Process

From DuPont Web site



Interactions
Concentration
Matrix fluid
Flow conditions

different dispersions

Deficiency in any stage leads to POOR DISPERSION CONTROL

Dispersion impacts appearance, durability, functionality

Current Methods for Dispersion Measurements

- Fineness of grind gauge
  - Screening for micron-size particles
- Particle size by light scattering in very dilute state
  - Dilution shock, not equivalent to concentrated state
- Microscopy (SEM and TEM)
  - Limited sampling area, destructive, labor intensive
- Viscosity, optical density, color and tinting strength
  - Indirect, subjective

- non-quantitative, inadequate, inefficient-

What We Need!

✓Understanding how particles/pigments **can be dispersed in a wide variety of media will be key to the adoption of many materials** by commercial markets

Characterize Dispersions

Understand Dispersion Mechanisms

Predict Dispersed State

Control dispersion

✓**Characterizing multi-scale structure of the materials and relate to the performance/service life of the products.**

Heterogeneity ? at what length scale ?

Correlation and impact?

New Idea and Approach

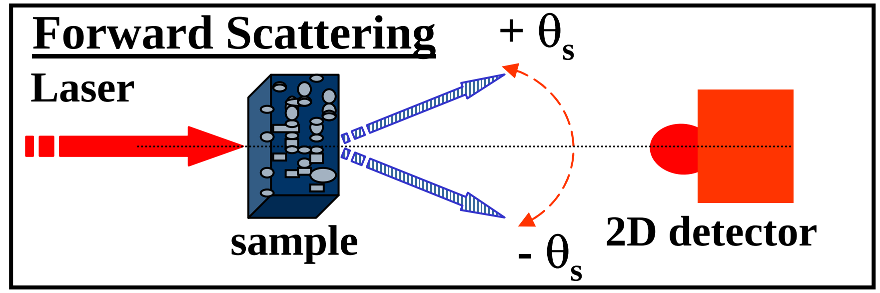
- Using existing methods (microscopy and SANS..) and knowledge– with faster and better analysis methods/computer processing
- New instrument and capability (LS) in BFRL
- New approach and metrology
  - diffusive methods
  - backscattering
  - multi-wavelength application

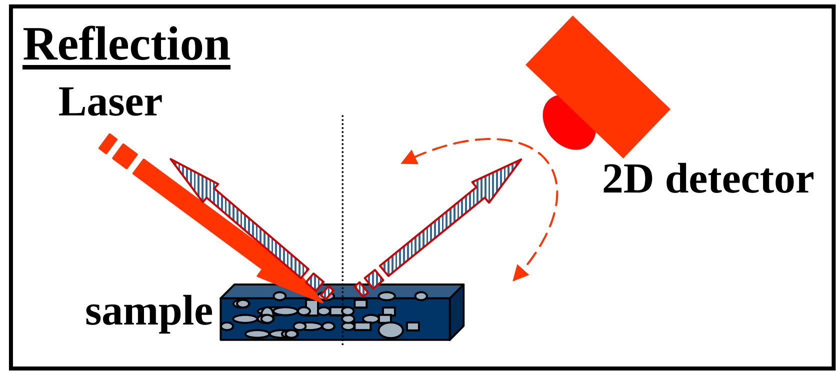
Using photonic, acoustic, neutron, and other sources

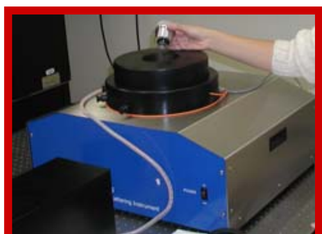
Light Scattering Materials Characterization Laboratory

A308/226

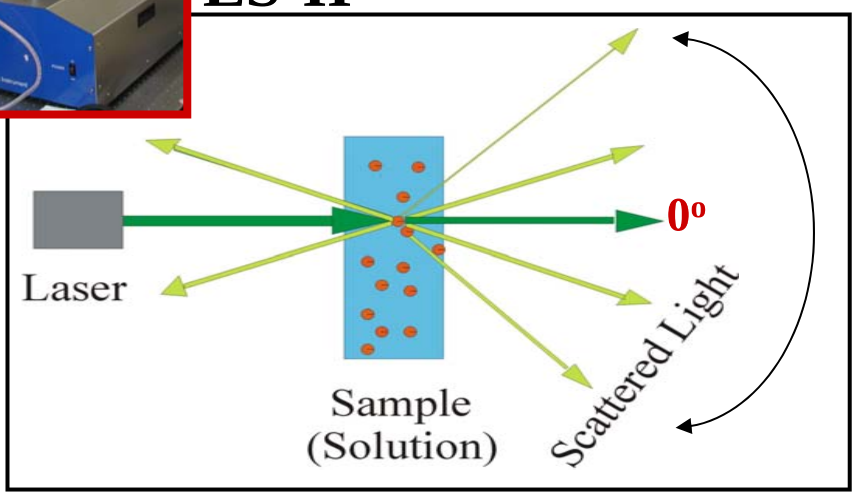
LS-I





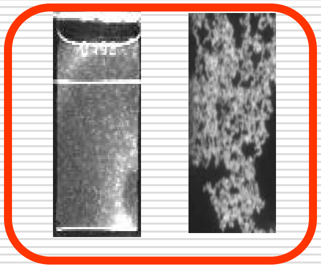


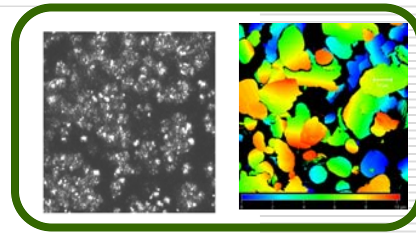
LS-II



- Static (5 nm – 10 mm)
  - Time-averaged
- Dynamic (1 nm – 5 mm)
  - Time-dependent
- Angular range (5^o to 175^o)
- Temperature (0^o to 100^o C)

Measurable Materials Properties





liquid, suspension

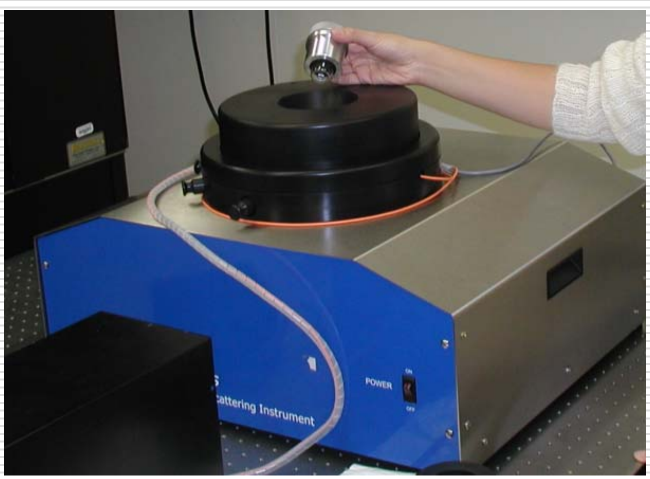
Processing condition

solid, film

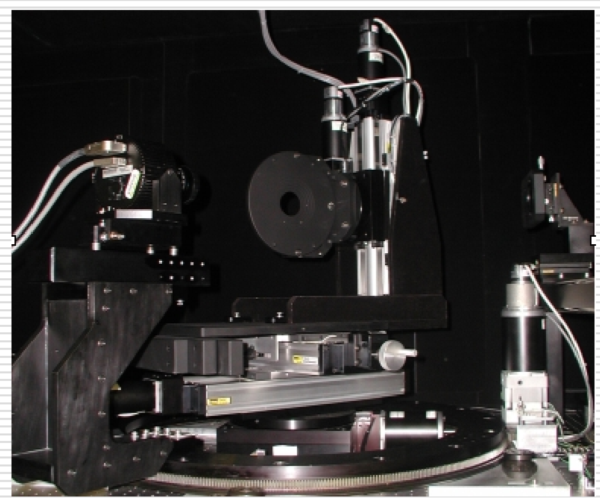
- Spatial distribution of each constituent
- Interaction among each constituent
- Pigment/nanoparticle cluster size and dispersion

- Bulk/surface morphology
- Nano-/Microstructure
- Appearance (gloss & color)

LS-II



LS-I



Technical Approach -Research Objectives

- Develop non-invasive, quantitative, and scientific-based metrologies for characterizing particle dispersion in suspensions and in solid polymeric films

- Relate these dispersion properties to the appearance and service life of polymeric materials.

→ "What dispersion state" gives "best" performance.

- Establish measurement protocols for quantitatively measuring particle dispersion in suspensions and coatings.

Dispersion Project Organization

Characterization

- Degree of dispersion, flocculation
- Size and shape of aggregation
- Spatial distribution of aggregation
- Particle-particles interaction
- Particle-media interaction

Modeling Input
With Nicos Martys, BFRL

Systems

Pigments/Nanoparticles
in
Power, Film, Resin, Liquid

Processing & Modification

- Mixing process
- Pigment surface treatment
- Surfactant addition
- In-situ polymerization
- Sol-gel reaction

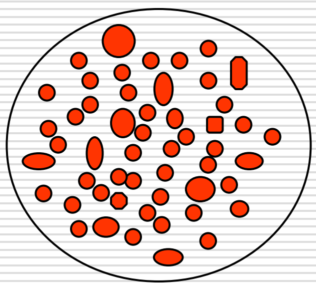
Impact on

- Optical properties (appearance)
- Morphology, surface properties
- Photodegradation
- Photoreactivity
- Mechanical properties

Working with Xiaohong Gu, Stephanie Watson, Aaron Forster, and Tinh Nguyen

Measurement Organization

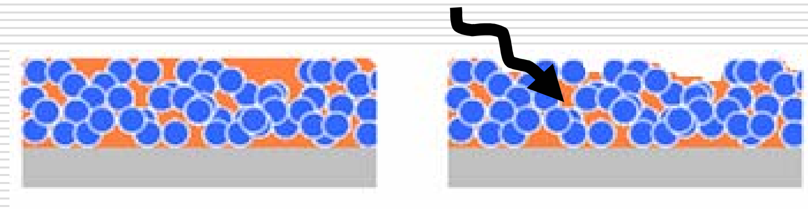
In suspensions



Light scattering
Neutron scattering

In film and bulk

(before and after UV degradation)



Microscopy (LSCM, ESEM)
Light scattering
Neutron scattering
Depth profile sensitive tools

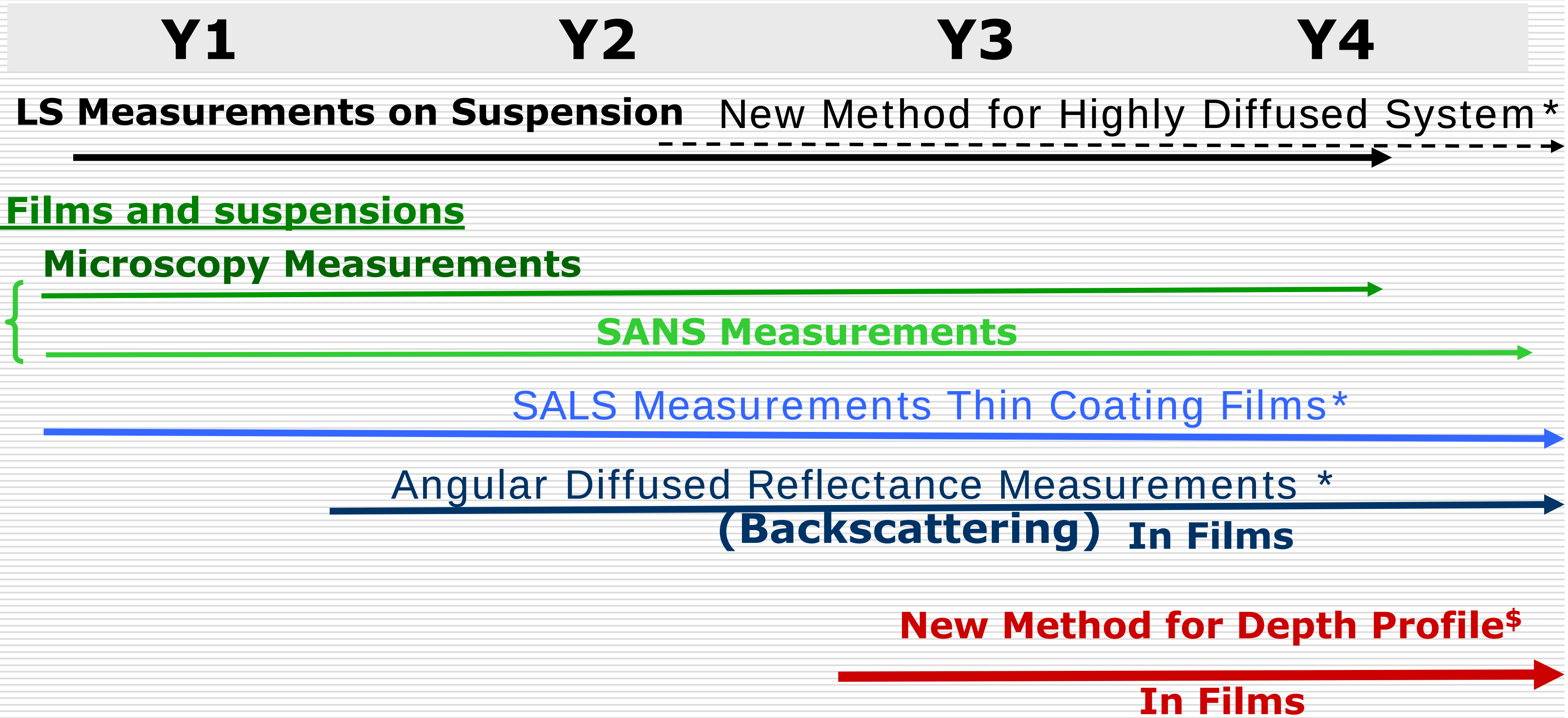
Tools

Concentration
Flocculation
Size Distribution
Interaction

Dispersion Parameters

Pigment volume concentration
Size and structure of agglomerates
Spatial distribution
(lateral and vertical)

Results Generated: Gantt chart

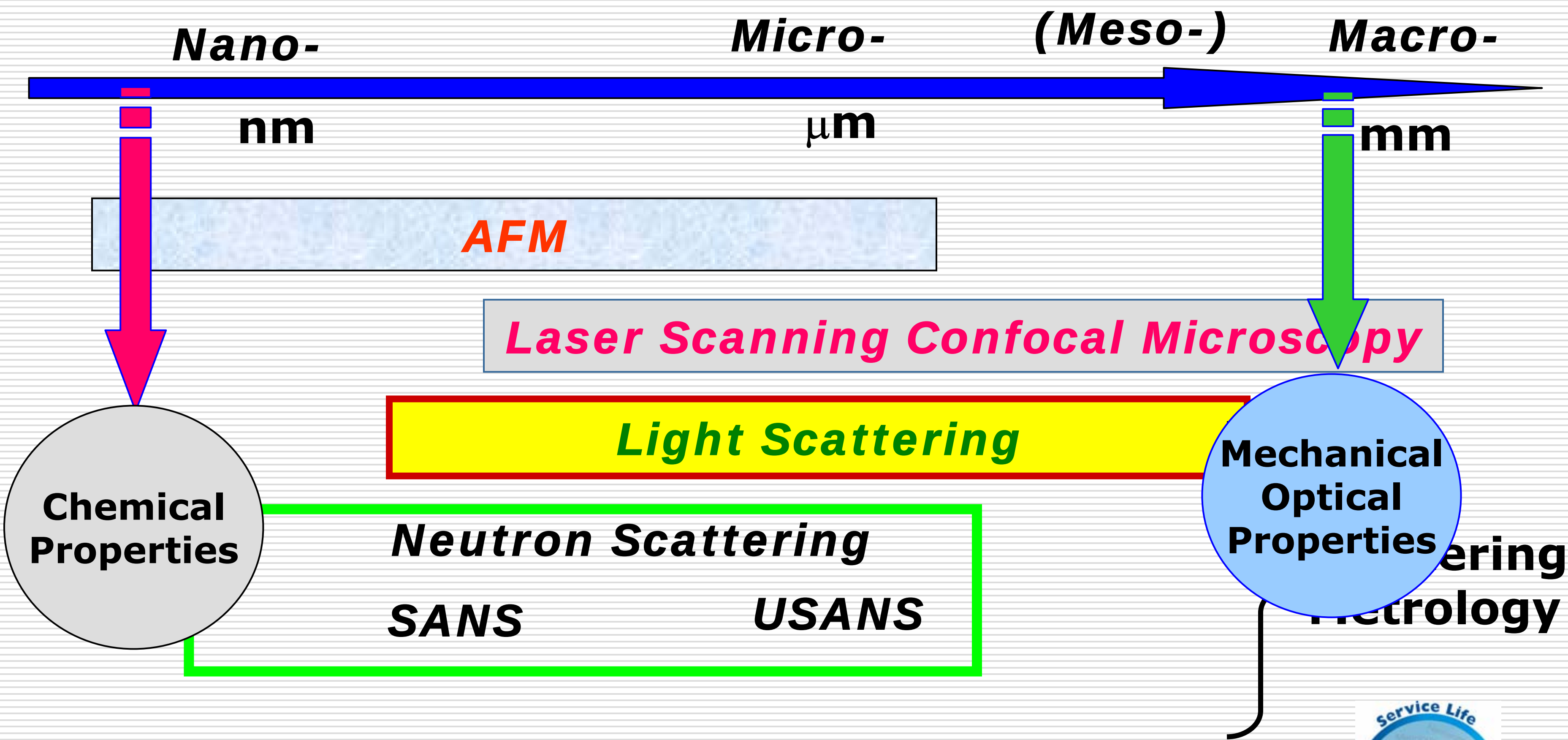


Refine and improve current measurement techniques and advance data analysis

***: Need new high power laser/light source, detector, and optics**

$: Invest on new instrumentation

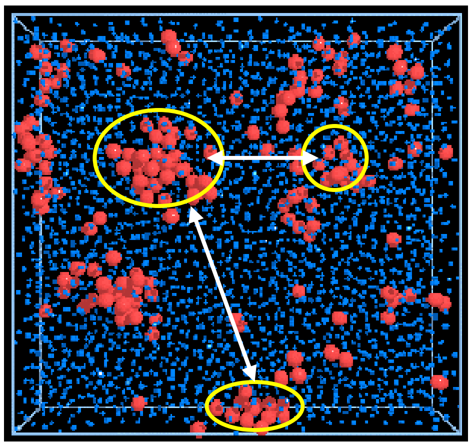
Multi-Scale Characterization Techniques



For Bulk/Surface Morphology, Microstructure and Dispersion

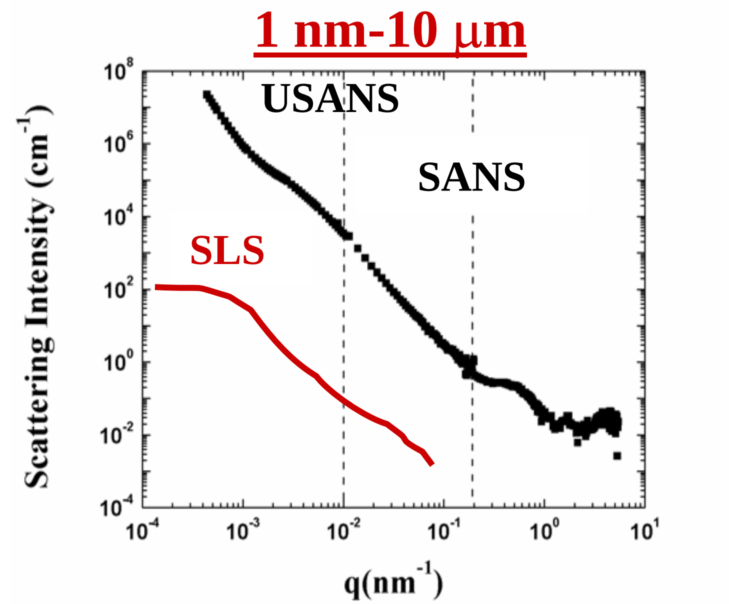
Particle Dispersion Characterization
- Scattering Metrology-

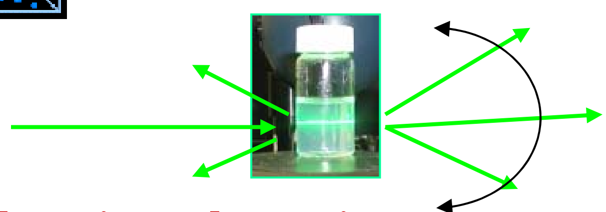
Structural Properties



Static and Dynamic

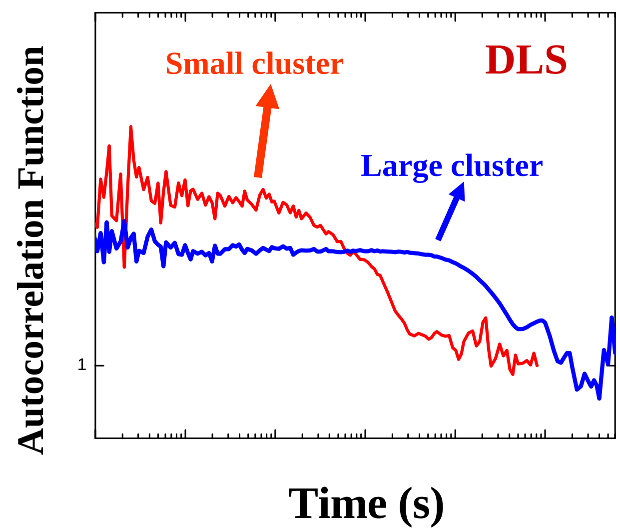
- ✓ Cluster Size & Shape
- ✓ Cluster-Cluster Interactions
- ✓ Morphology
- ✓ Spatial Distribution





Metrology

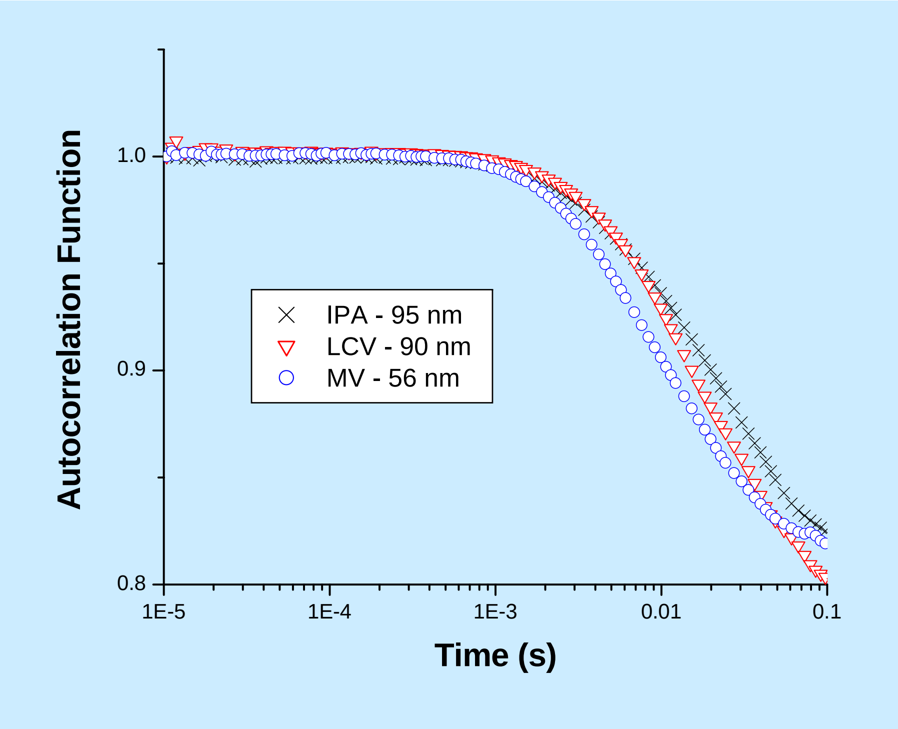
- ❑ Angular-resolved static & dynamic light scattering (SLS &DLS)
- ❑ Ultra-small & small-angle neutron scattering (USANS & SANS)
- ❑ Ultra-small & small-angle X-ray scattering (USAXS & SAXS)



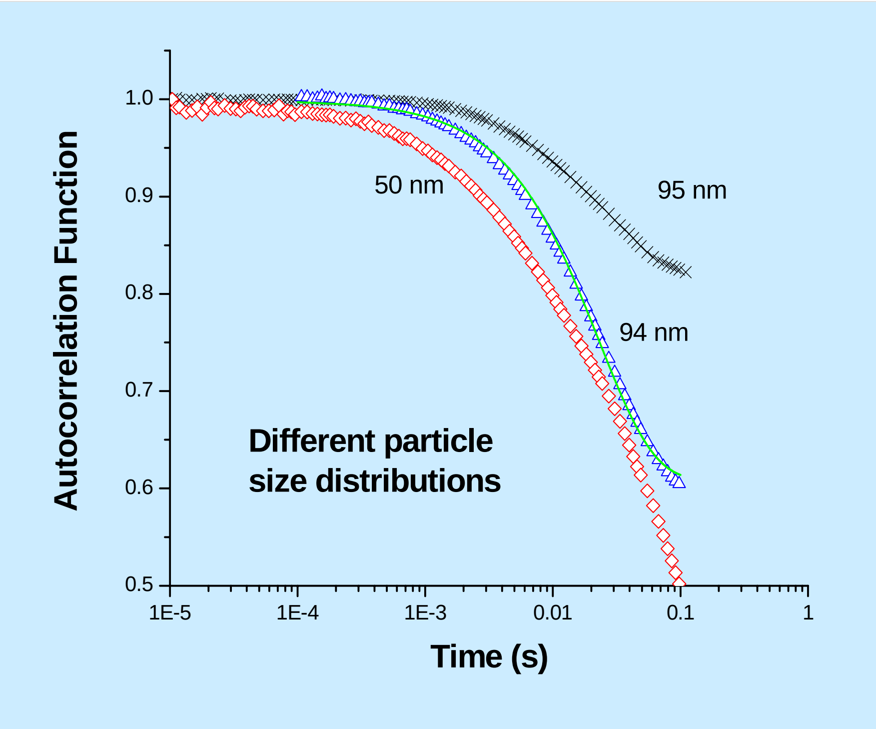
Cluster Size Characterization of TiO_2 Particles in Various Chemical Assays

DLS

Three chemical Assays



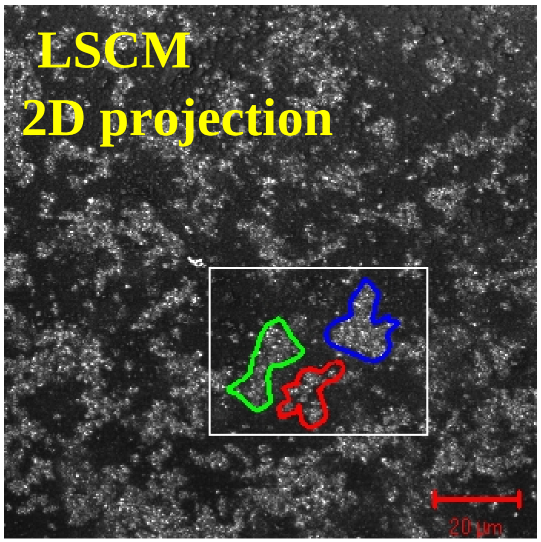
Three particle sizes & surface treatments

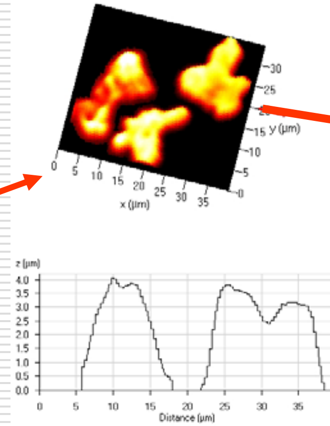


Study the correlation of "*particle size, types, surface treatment*" to photoreactivity of TiO_2 particles

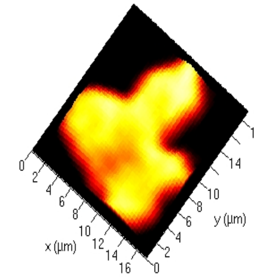
Size and Dispersion of Pigment Clusters

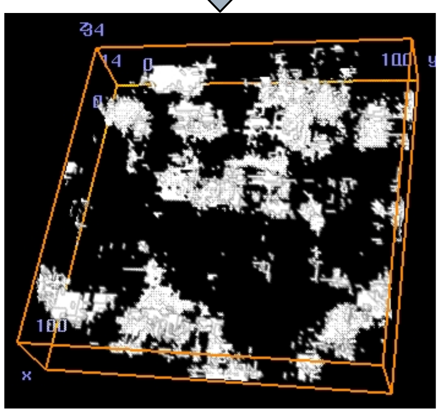
LSCM & SANS



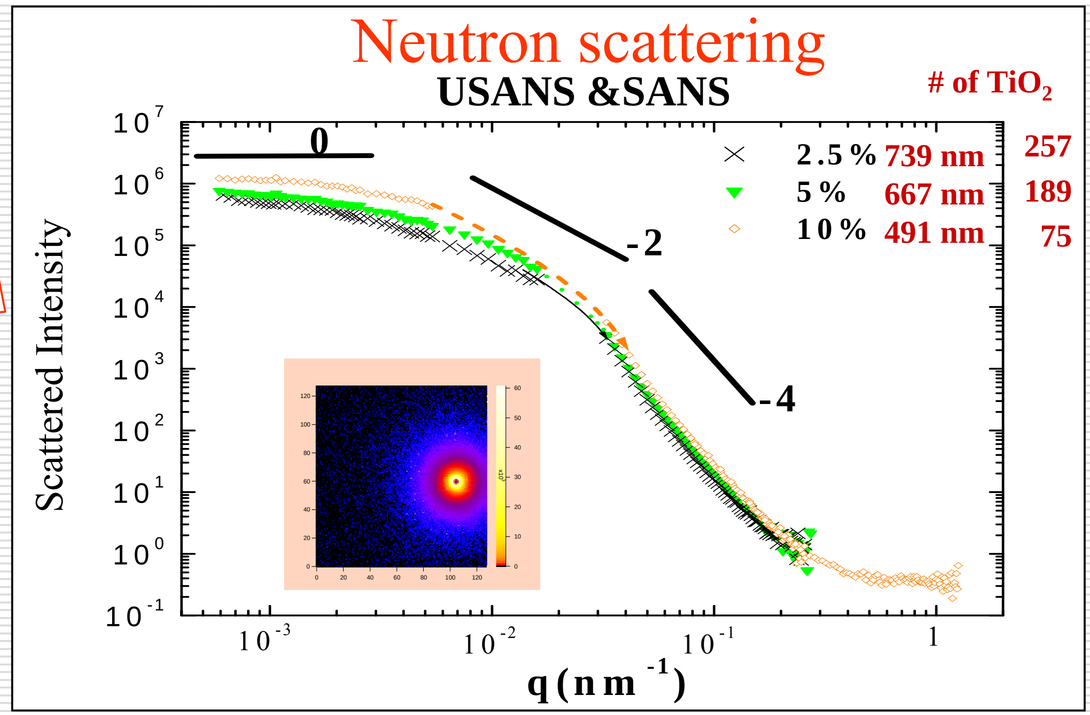


Topographic analysis



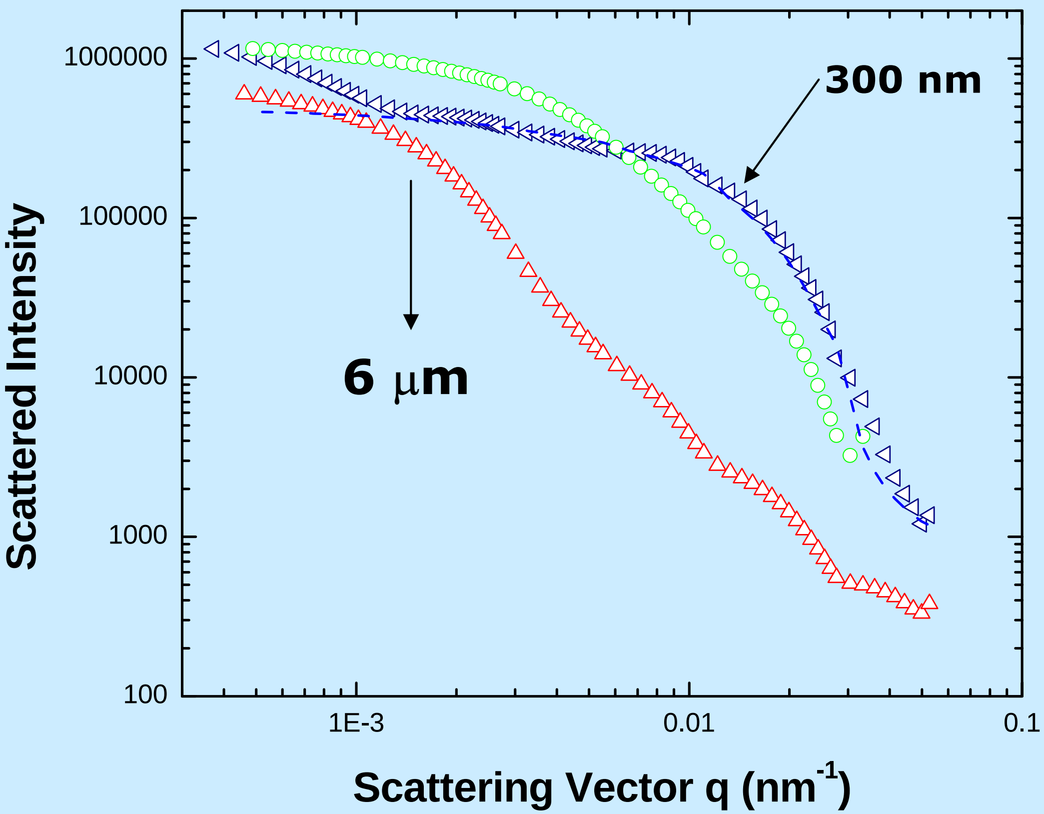


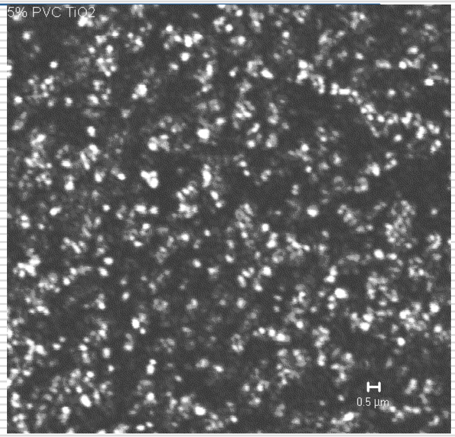
3D reconstruction

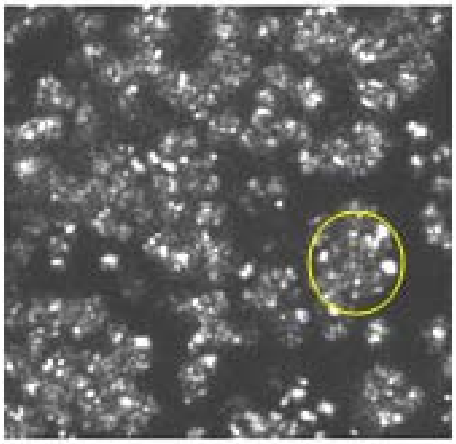


Pigment Dispersion in Polymer Coatings

- different media, different processing -





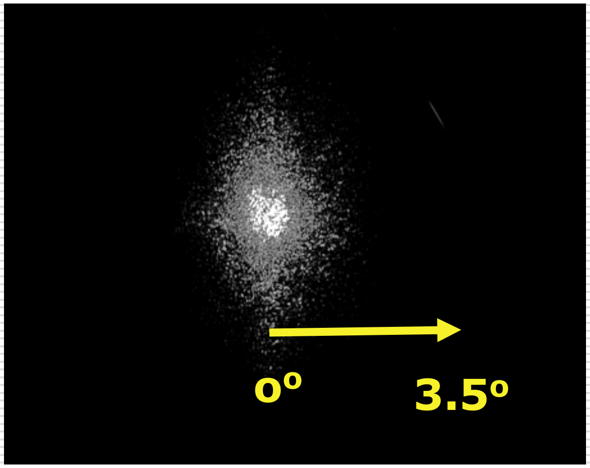


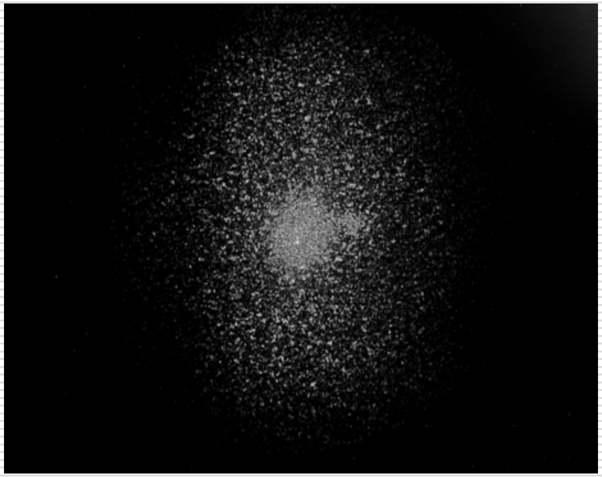
2 μm

Pigmented epoxy, latex coatings

Small Angle Light Scattering (SALS) from Latex $-TiO_2$ Coatings

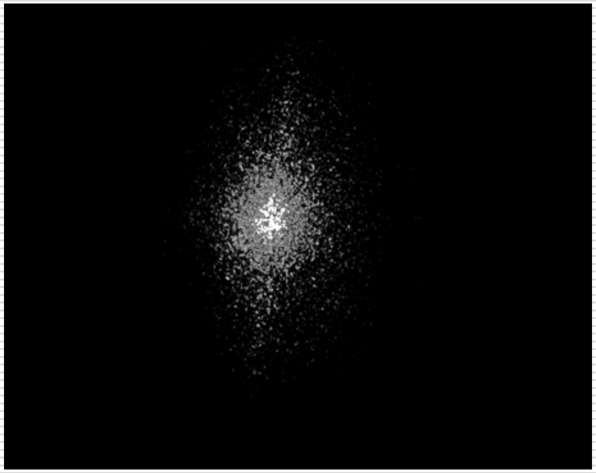
0 %

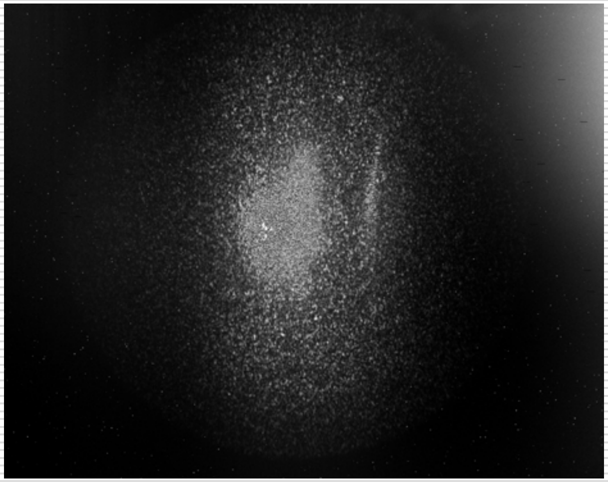




17 %

2.5 %



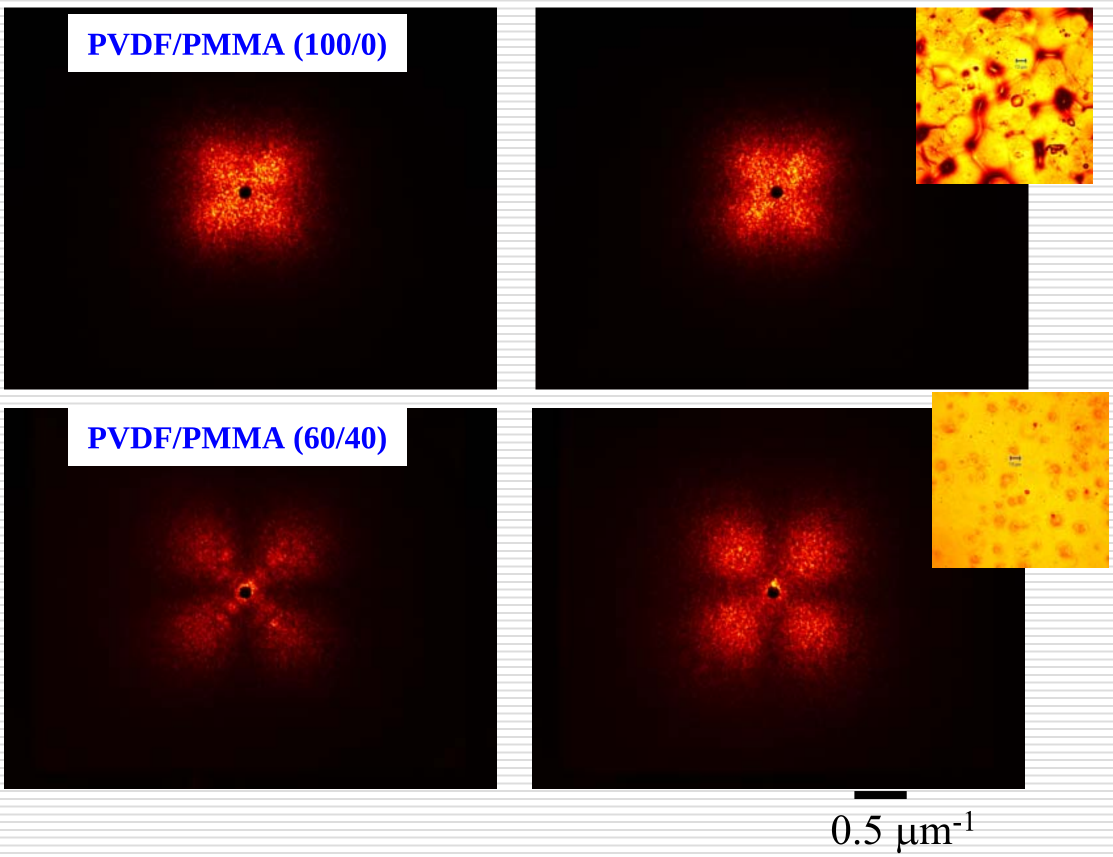


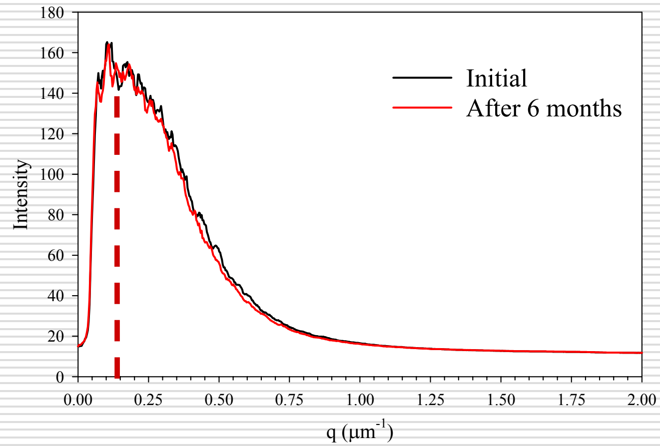
17 %
larger
pigment

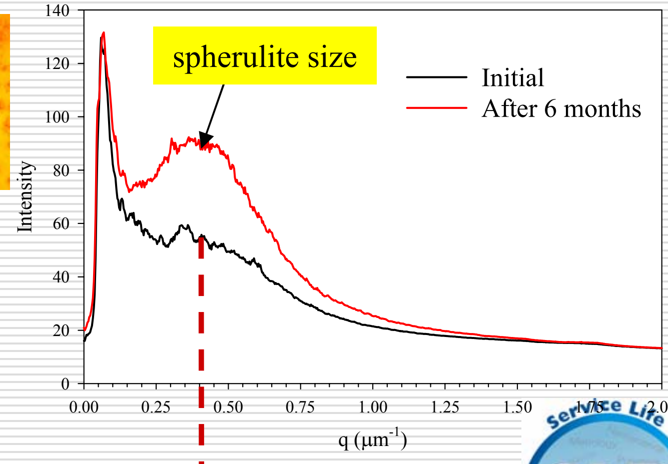
Optical scattering profiles reveal different structures in latex coatings

Small-Angle Light Scattering Study of UV-degraded PVDF Coatings

Initial **After 6 months-UV**

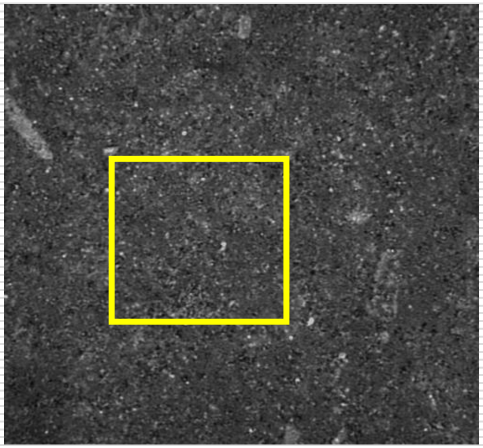


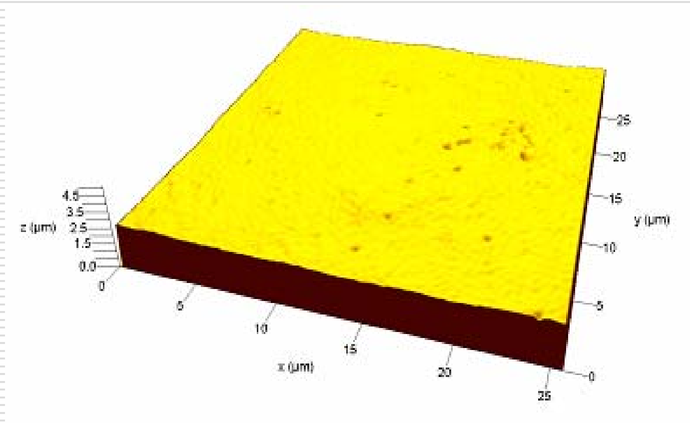


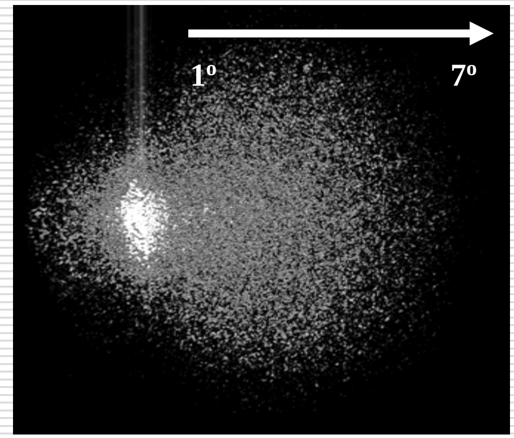


Diffuse Scattering from Weathered Surfaces

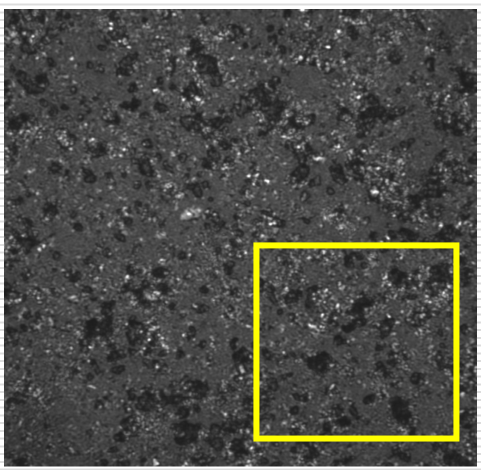
Masked LSCM **Masked**

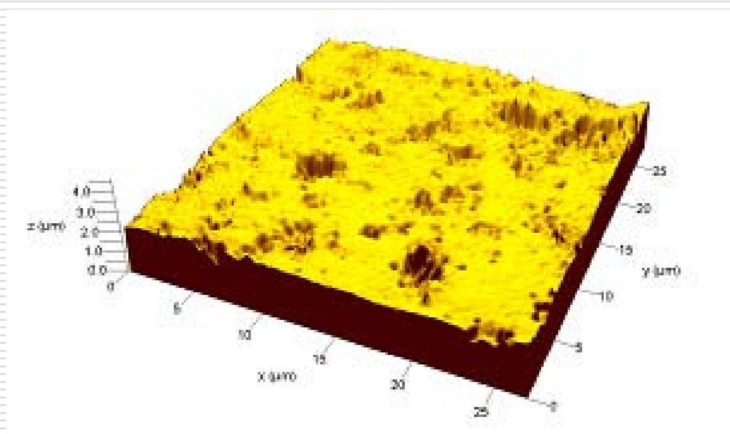


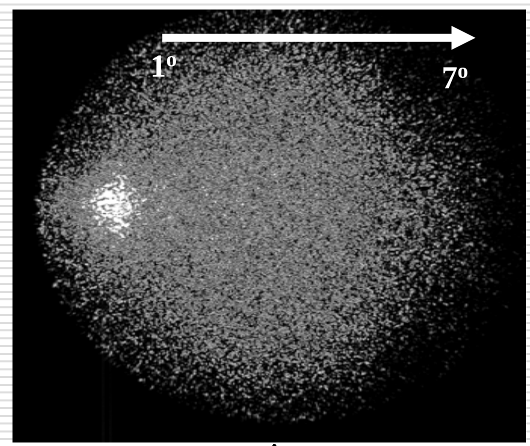




Exposed **Exposed**

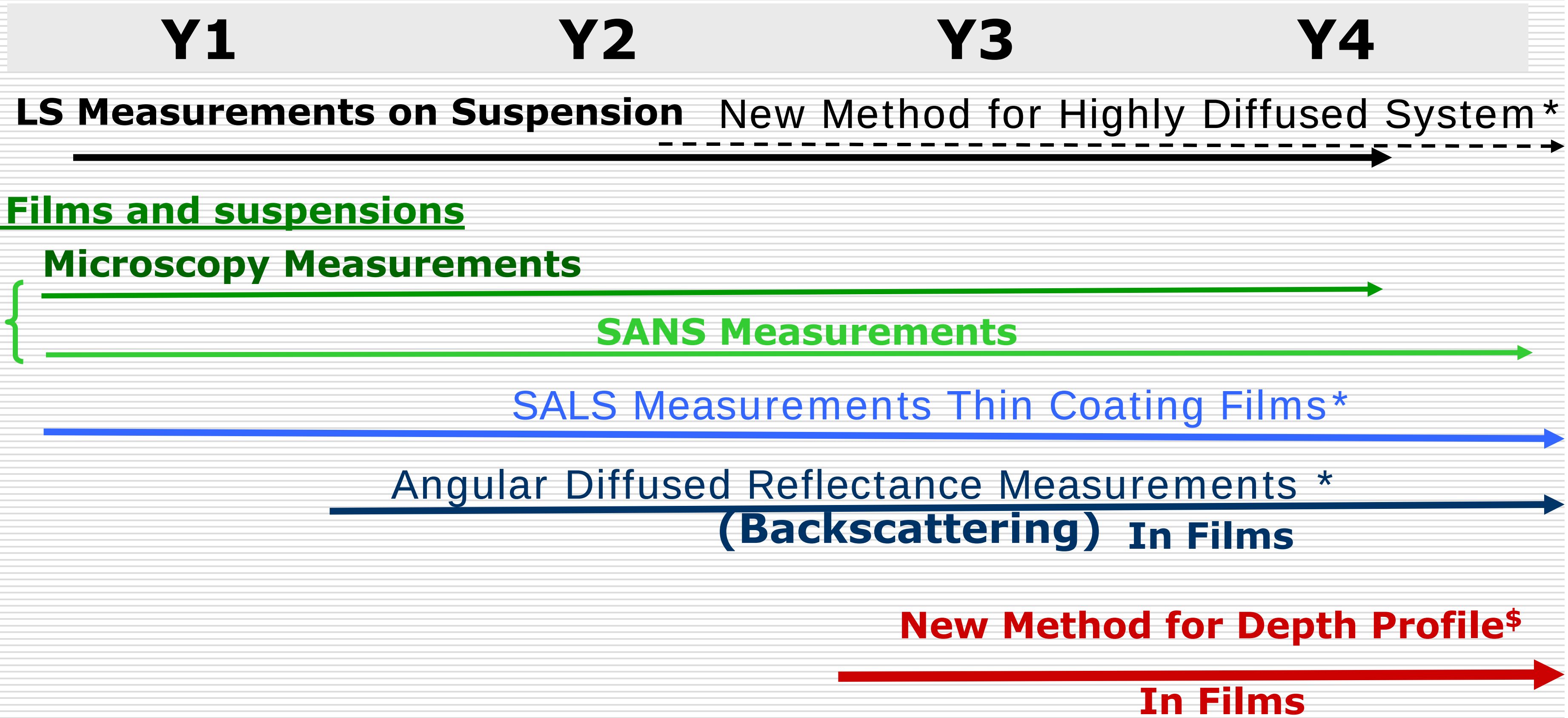






Specular intensity ⇓ ; diffuse scattering ⇑

Results Generated: Gantt chart



Refine and improve current measurement techniques and advance data analysis

***: Need new high power laser/light source, detector, and optics**
$: Invest on new instrumentation

Impact

- Provide a unique and critical understanding of the particle dispersion in polymeric systems, one of the key components in future pigment/nanoparticle products and technologies.

- Optimize the pigment dispersion in coatings to achieve best performance, significantly reduce the costs associated with materials and production process.

- Provide in-depth knowledge in dispersion mechanism to industry for production and improve appearance and service life performances